

An Optical Method of Measuring Vapour Pressures : Vapour Pressure and Apparent Superheating of Solid Bromine.

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In the course of an investigation of the refractivity of gaseous bromine conducted with a Jamin refractometer it was observed that, as the temperature changed, very slight variations of the density of the vapour could be quickly and accurately recorded. This fact suggested that an optical method would be useful for measuring vapour pressures or densities at low pressures, especially in the case of substances which attack mercury. The following observations on the vapour of bromine serve as an illustration of the possibilities of the method, and have brought to light an interesting phenomenon, which is described below.

A thin glass bulb, containing 1 or 2 c.c. of Kahlbaum's pure bromine, was sealed to a tube communicating both with the pump and the refractometer tube. The temperature of the bromine was reduced to -80° C., at which its vapour pressure is negligible, and the bulb was completely evacuated, so as to remove all traces of hydrobromic acid which might have formed by the action of the bromine on the tap-grease since the previous experiment. The refractometer tube was separately evacuated, and the two were put in connection by opening a tap. The cooling bath was then slowly brought up to atmospheric temperature by stages, while an observer counted the interference bands which crossed the field of view of the refractometer.

During each reading the temperature of the bulb was kept constant by stirring the bath. As the melting-point was approached numerous readings were taken, the rise of 1° from -8° to -7° sometimes occupying 20 minutes. A complete series of readings between -80° and 0° occupied about an hour. At the moment of each reading the temperature of the refractometer tube was also read. The light used was approximately monochromatic, and had the wave-length of the red Cd line, 6438.

In this experiment what is actually observed is the temperature of the liquid bromine and the corresponding refractivity of the vapour in the refractometer tube, which is at the same pressure as the vapour in contact with the liquid, though at a different temperature. The refractivity of bromine vapour for a known density had previously been determined by us,

and if we assume that the refractivity is proportional to the density, as Mascart's work justifies us in doing, then the density of the vapour in the refractometer tube is known for various temperatures. It may further be assumed that, at the low pressures at which measurements were taken, the pressure of the vapour in the tube is proportional to its density. Hence, if we know one pressure and temperature absolutely, the whole curve of temperatures and pressures can be calculated from these observations.

Ramsay and Young* found for bromine at its melting point a pressure of 44·5 mm.

Assuming this value, the table below shows the vapour pressures derived from a typical set of readings which are well supported by other series.

Vapour Pressures of Solid Bromine.

Temp. (C.)	Pressures (mm.)			Temp. (C.)	Pressures (mm.)		
	Observed.	Calculated.	Difference.		Observed.	Calculated.	Difference.
-80°	0·13	0·13	0	-15°·7	22·9	22·34	-0·56
-64°·75	0·52	0·43	-0·09	-15°·1	24·35	23·44	-0·91
-63°	0·66	0·5	-0·16	-12°·7	28·8	28·41	-0·39
-59°·9	0·79	0·65	-0·14	-12°·5	29·9	28·87	-1·03
-53°·3	1·05	1·1	+0·05	-10°	36·15	35·27	-0·88
-46°·9	1·83	1·83	0	-9°·6	37·1	36·42	-0·68
-41°·3	2·89	2·87	-0·02	-7°·7	42·25	42·41	+0·16
-28°·8	7·74	7·82	+0·08	-7°·5	42·9	43·1	+0·2
-28°·3	8·14	8·14	—	-7°·2	43·9	44·14	+0·24
-22°·6	13·0	12·82	-0·08	-7°·1	44·5	44·5	—
-19°·4	16·7	16·61	-0·09				

If the values of p are plotted against the absolute temperatures the points fall on an exponential curve

$$p = ab^{\theta},$$

where

$$a = 2·485 \times 10^{-8} \quad \text{and} \quad b = 1·0834.$$

The values of p , calculated from this equation, are shown in the third column. The constants were derived from the values $p = 44·5$ and $8·14$. At $-12°·74$ C., Ramsay and Young found $p = 28·1$ mm. The number calculated from the formula above is $28·3$. At $-17°·12$ they found $p = 18·9$ against $19·9$ calculated. Thus the two sets of observations agree well.

Numerous observations were taken at and about the melting point, both with ascending and descending temperatures, and on several occasions, though not on all, an interesting fact was observed. With steadily rising temperature of the bath the vapour pressure at the melting point increased

* 'Chem. Soc. Journ.,' vol. 49, p. 457.

above 44.5 mm. by 1 or $1\frac{1}{2}$ mm., and then, in the course of one or two minutes, fell back again. After remaining almost constant for a few seconds it then began to jump several times and fall back again, and at last it mounted steadily and rapidly. At each jump, which lasted one or two seconds, the pressure rose by 1 or 2 mm.

A corresponding result was observed with falling temperature of the bath, the vapour pressure suddenly rising and then decreasing, but without jumping.

These phenomena may possibly be due to differences of temperature between neighbouring portions of the solid in the bulb, vapour being formed at one place and condensed in another. But they are more probably explicable as the changes which might be expected to occur during the superheating of the solid and supercooling of the liquid. The superheating of a solid is stated by Chwolson to have been observed by Barus in the case of naphthalin; and Duhem gives instances of a similar phenomenon in connection with the passage of a solid from one crystalline form to another.

Whatever be the cause, the optical method seems to promise a valuable means of investigating the rapid and delicate changes of vapour pressure which must occur at the freezing point. Jamin's form of interferometer is, of course, not indispensable. The simple design described by Lord Rayleigh, and used by Ramsay and Travers for the inert gases, would prove equally efficient.
